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TECHNICAL NOTE 2198

SINTERING MECHANISM BETWEEN ZIRCONIUM CARBIDE AND COLUMBIUM

By H. J. Hamjian and W. G. Lidman

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NACA

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SINTERING MECHANISM BETWEEN ZIRCONIUM CARBIDE AND COLUMBIUM

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SUMMARY

An investigation was made of the sintering process and the sintering mechanism of a zirconium carbide - columbium ceramal (12.5 percent by weight of columbium). The specimens used were prepared by hot-pressing and the effects of sintering temperature and time at temperature on the structures were determined. A bonding study was also made of a hot-pressed zirconium carbide specimen and columbium powder.

The results of the investigation indicated that the sintering mechanism is one in which columbium atoms diffuse into the zirconium carbide lattice, displace zirconium atoms, and form columbium carbide and zirconium metal. This columbium carbide is completely soluble in the matrix of zirconium carbide and a homogeneous solid solution of the carbides is formed. At the sintering temperature of 3900° F, the zirconium metal forms in the grain corners of the carbide structure.

Size and distribution of the metal phase could be controlled by two sintering variables, temperature and time at temperature. The specimen with a fine dispersion of metal has the highest strength.

INTRODUCTION

Sintering is the fundamental process in the establishment of the structure and properties of a ceramal; a study of the sintering mechanism is therefore helpful in the fabrication of a body with optimum properties. Most of the published work concerning the theory of sintering ceramals has been done on cemented carbides of the tungsten carbide - cobalt type. With this material, sintering takes place in the presence of a liquid and the metal facilitates the growth of carbide crystals (reference 1). Other mechanisms of sintering a ceramal depend on the materials and the area of the particular phase diagram in which sintering takes place.

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Metal additions to a ceramic are being considered because there is a possibility of improving the thermal-shock resistance and of lowering optimum fabrication temperature of the pure ceramic; there may, however, be a loss in refractoriness. A ceramal consisting of zirconium carbide and columbium is of interest because both constituents have high melting temperatures and, in addition, zirconium carbide has a high tensile strength at 2200° F (reference 2). In order to study the sintering mechanism of this ceramal, an investigation was therefore conducted at the NACA Lewis laboratory.

A bonding study was made using a hot-pressed zirconium carbide specimen and columbium powder in order to determine the compatability of these materials. Lattice-parameter measurements by X-ray diffraction, microstructure studies, density measurements, and room-temperature modulus-of-rupture evaluations were used to establish the sintering conditions and to investigate the sintering mechanism. Specimens used in this investigation were prepared by hot-pressing and the effects of sintering temperature and time at temperature were studied.

APPARATUS AND PROCEDURE

Materials

Powders used as the component materials of the ceramal under investigation were obtained commercially. The purity of the columbium (Cb) is 99.8 percent. The calculated percentage by weight and the chemical analysis of the zirconium carbide (ZrC) powder are presented in the following table:

	Calculated weight (percent)	Chemical analysis (percent)
Zirconium	88.37	85.13
Carbon	11.63	12.58
Columbium	-----	.22
Titanium	-----	.48
Iron	-----	.03

The mesh sizes of the columbium and the zirconium carbide were -400 and -325, respectively. The columbium powder was stored in a moist state in order to reduce the fire hazard during handling.

Preparation of Bonding Specimen

A study of the bonding mechanism between columbium and zirconium carbide was made by placing columbium powder in an indentation ground in a specimen of hot-pressed zirconium carbide (reference 3). Before the experiment, the carbide was washed in carbon tetrachloride, in dilute hydrochloric acid, and finally in distilled water. The specimen containing the powder was placed on a graphite block in a zirconia crucible wound with tungsten wire. The crucible was then placed within an induction coil in a vacuum chamber evacuated to a pressure of 10 microns prior to heating. The graphite block and tungsten wire were heated by induction that in turn heated the specimen to 4250° ±50° F, which is near the melting point of columbium. The specimen temperature was measured with an optical pyrometer by sighting through the quartz window mounted in the top of the vacuum chamber. Above 3400° F, a small amount of argon was passed across the inner surface of the quartz window in order to prevent clouding. The specimen was held at temperature for 15 minutes and the power was then cut off. After furnace cooling to room temperature, the bonding specimen was sectioned through the indentation, mounted in bakelite, and prepared for microscopic examination by polishing the surface with diamond abrasives.

Preparation of Sintered Specimens

Combining powders. - A charge consisting of 425 grams of zirconium carbide and 75 grams of moist columbium were combined by mixing in a 1-quart porcelain jar mill; 10 porcelain balls were added to facilitate the mixing action. A slurry of powders was formed by adding ethyl alcohol to fill the jar, which was sealed and rotated at 40 rpm for 48 hours. After completing the mixing operation, the contents of the jar were filtered to remove the excess liquid, air-dried for 24 hours, and then stored in tightly sealed glass jars until ready for use. Chemical analyses of the powder mixtures are given in the following table:

Mixture	Zirconium (percent)	Columbium (percent)	Carbon (percent)
4MC	75.36	11.16	11.76
5MC	73.82	12.29	11.55
6MC	73.82	12.54	10.92
7MC	73.65	12.37	10.80
9MC	73.44	12.83	10.17

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Hot-pressing. - In this investigation, disk-type specimens of $1\frac{13}{16}$-inch diameter and approximately 1/4-inch thickness were obtained by hot-pressing. The specimen chamber of the graphite dies used was $1\frac{13}{16}$-inches in diameter; outer dimensions of the die were 6 inches in diameter and 5 inches long. An induction coil powered by a 50-kilowatt induction unit was used for heating the die.

Sintering temperatures were measured with an optical pyrometer by sighting between two adjacent loops of the induction coil into a 3/8-inch-diameter hole that was drilled 1-inch deep into the graphite die at the midsection. A load was applied to the specimen by a hydraulic jack mounted vertically above the die plunger and a pressure gage, which measured the line pressure between the hydraulic pump and the jack, was used to measure the load exerted on the die plunger.

A load of 2000 pounds per square inch was applied and the die was heated to the sintering temperature by using 40 kilowatts of power. As the desired sintering temperature was reached (about 1/2 hr was required), the power was adjusted to maintain a constant temperature. In order to determine the effect of temperature and time at temperature, specimens were sintered at 3700°, 3900°, and 4050° ±30° F for 5 minutes and at 3900° ±30° F for 15, 30, 45, and 90 minutes. The die was allowed to cool in air to room temperature before the specimen was removed; the time required was about 3 hours.

A representative chemical analysis of a specimen before and after sintering, which shows that no carbon was picked up in the process, is:

Sintering	Zirconium (percent)	Columbium (percent)	Carbon (percent)
Before	73.82	12.29	11.55
After	74.71	12.90	11.23

Evaluation of Sintered Specimens

X-ray study. - In order to determine the effect of temperature and time on the lattice of the sintered specimens, X-ray diffraction patterns were taken of representative specimens at each temperature and time investigated. Copper Kα and Kβ radiation with a Sachs type back-reflection camera and a film-to-specimen distance of 3 centimeters were used.

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Microscopic examination. - Studies of the structure of representative samples were made using standard metallographic methods. Specimens were prepared using polishing wheels and diamond abrasives.

Density measurements. - Density measurements were made in order to determine the uniformity of specimens. Differential weighings in air and water were made with an analytical balance and the individual values are believed to be correct to within ±0.01 gram per milliliter.

Modulus-of-rupture determination. - Evaluation of modulus of rupture was made in order to determine the sintering conditions. Hot-pressed specimens were cut in such a way as to furnish two rectangular modulus-of-rupture specimens approximately $1\frac{1}{2}$ inch long, 1/4 inch thick, and 1/2 inch wide. All of the surfaces of these pieces except the ends were longitudinally ground using resinoid-bonded diamond-embedded grinding wheels.

The two types of three-point loading apparatus used for modulus-of-rupture evaluations at room and elevated temperatures are similar to those used in reference 4. The elevated-temperature modulus-of-rupture apparatus consisted of a commercial globar resistor furnace into which a lever-loading system and a protective atmosphere chamber had been incorporated. During heating and evaluation periods, the specimen and the portion of the modulus-of-rupture apparatus in the furnace were enclosed within the chamber through which argon flowed at the rate of 30 cubic feet per hour. Specimens were supported on silicon carbide knife edges cemented to a refractory brick and were loaded at a rate that gave a stress increase of 2000 pounds per square inch per minute in the extreme outer fiber at the midpoint of the specimen length. Temperature of the specimen was measured by a chromel-alumel thermocouple at 2000° F and by a platinum - platinum 13-percent rhodium thermocuple at 2400° F. After the specimen was placed on the supporting knife edges, 10 minutes were allowed for the specimen to heat to the evaluation temperature before loading was started. Modulus-of-rupture evaluations were conducted at 2000° and 2400° ±10° F.

Modulus of rupture was calculated from the following equation, which is derived from the standard beam formula:

$$S = \frac{3}{2}\left(\frac{pd}{wt^2}\right)$$

where

S modulus of rupture, pounds per square inch

p load on specimen (measured load times lever ratio), pounds

d distance between supporting knife edges, inches

w specimen width, inches

t specimen thickness, inches

RESULTS AND DISCUSSION

Study of Bonding Specimen

After heating the bonding specimen for 15 minutes at 4250° F, the columbium melted and when cooled, the metal adhered to the carbide; visual examination showed no evidence of oxidation. The microstructure of the specimen (fig. 1) shows columbium, zirconium carbide, and the position of the original interface. Light-gray particles at the interface are probably oxides that were formed during heating. In addition, the photomicrograph shows that columbium and zirconium carbide adhere and diffusion appears to have taken place. In order to fabricate a strong body of zirconium carbide and columbium, the powdered constituents must be mixed and heated to a temperature at which equilibrium between the phases will be established within a reasonable length of time.

Study of Sintered Specimens

In order to determine the effect of temperature on the lattice parameter of the carbide in the sintered specimens, calculations were made from back-reflection patterns reproduced in figure 2. For comparison, a pattern of zirconium carbide of the composition previously given in the section "Materials" is also included in the figure. The lattice parameter of the zirconium carbide, which has a sodium chloride-type crystal structure, was found to be 4.686 A, which agrees with the lattice parameter reported in reference 5. With the composition investigated, no columbium lines were detected; any observed change during sintering would therefore result in a change in the zirconium carbide lattice.

The effect of temperature on the lattice parameter of sintered zirconium carbide and approximately 12.5 percent by weight of columbium are:

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Specimen	Sintering time (min)	Sintering temperature (°F)	Lattice parameter (A)	Remarks
ZrC	5	4100	4.686	
4MC1	5	3700	4.686	Lines same as ZrC
4MC2	5	3900	4.652	Lines shifted and broadened
4MC3	5	4050	4.652	Lines same as 4MC2 but sharpened

The specimen sintered at 3700° F showed no change in the diffraction lines as compared with the zirconium carbide specimen, indicating that no reaction had occurred. The diffraction lines of the specimen sintered at 3900° F broadened and the lattice parameter changed indicating that a reaction between the two constituents occurred. Broadness of the diffraction lines suggests incomplete diffusion and implies that stresses induced by the reaction are still present. At 4050° F the lines were sharp indicating that the reaction between the constituents had reached equilibrium; by measurements, the lines were found to have the same spacing as those for the specimen sintered at 3900° F. These results showed that of the three temperatures investigated, 3900° F was the temperature at which sintering became rapid and, according to reference 6, major structural and property changes for this composition can be associated with this temperature.

The decrease in lattice parameter of zirconium carbide during the sintering process shows that an interstitial solid solution of zirconium carbide and columbium was not formed; however, a substitutional solid solution between the zirconium carbide and columbium might have occurred. Zirconium and columbium are transition elements and their atoms are of such a size that they both will form interstitial alloys with carbon (reference 7). The atomic radii of zirconium and columbium are approximately the same as the atomic radii of each metal in its monocarbide lattice (reference 8). When calculated from the distance of closest approach of the metal atoms in the carbide, the atomic radius of the zirconium in the zirconium carbide is 1.66 A, whereas the Goldschmidt atomic radius of the columbium atom corrected to a coordination number of 12 is 1.47 A. Difference in the size factor between the radius of the zirconium atom in the zirconium carbide and the element columbium is 11.4 percent, which is within the 15-percent size factor for solution of elements and is favorable for solubility, as stated in the Hume-Rothery rules (reference 9). Because columbium is a stronger carbide former than zirconium, it is reasonable to expect that columbium will displace the zirconium in the carbide to form columbium carbide and zirconium metal. The unlimited solubility between the carbides of columbium and zirconium is shown in figure 3.

If columbium (approximately 12.5 percent by weight) forms columbium carbide that goes into solid solution with the zirconium carbide, the percentage by molecular weight of columbium carbide in the solid solution thus formed is 15.7 percent. The lattice parameter of the composition corresponding to 15.7 percent by molecular weight of columbium carbide in solution is close to 4.652 A, which was the value determined in this investigation. On the basis of this discussion, the reaction during sintering of zirconium carbide and columbium probably occurs according to the equation

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$$Cb + ZrC \xrightarrow{heat} CbC + Zr$$

During sintering, as the zirconium is displaced by the columbium diffusing into the zirconium carbide lattice, a solution between zirconium and columbium is probably formed that becomes richer in zirconium with time and becomes depleted in columbium when the reaction is complete. Columbium carbide, which is formed during the reaction, is completely soluble in the matrix of zirconium carbide (reference 8) and a homogeneous solid solution of the carbides is formed. At the sintering temperature of 3900° F, the zirconium metal tends to fill the voids that exist in the sintered structure.

Unetched microstructures of the specimens sintered at various temperatures are shown in figure 4. These photographs show a matrix of zirconium carbide - columbium carbide solid solution, some metal particles, and some voids that are pores in the specimen or "pull outs" formed during grinding and polishing procedures. Comparison of figures 4(b) and 4(c) shows that the displaced zirconium coalesces (to attain a minimum surface energy) with increasing sintering temperature.

Effects of increasing sintering temperature on modulus of rupture and density of sintered specimens are shown in table I. The body sintered at 3700° F had low strength and density, the lattice parameter was not changed, and the microstructure shows improper sintering. Specimens sintered at 3900° and 4050° F had higher densities, the lattice parameter changed, and the microstructures appear similar except for larger particles in the solid-solution matrix of the specimen sintered at 4050° F. Modulus-of-rupture evaluation showed that the specimen sintered at 3900° F was stronger than the one sintered at 4050° F, thus indicating that lower strength occurs with the larger coalesced metal inclusions.

Based on these results, the time variable of sintering was investigated at a sintering temperature of 3900° F. In figure 5, X-ray

patterns, which were used for measurements, of the specimens sintered at 3900° F for 5, 15, 30, 45, and 90 minutes are reproduced. Lattice-parameter calculations for the specimens showed no change from the value reported earlier (4.652 A) and the reaction was therefore completed between the constituents in 5 minutes at 3900° F. The X-ray pattern for the specimen sintered at 3900° F for 15 minutes shows that broadness in the lines, probably caused by incomplete diffusion and by stresses induced into the specimen as a result of the reaction, has been eliminated.

As shown in figure 6 and table I, the highest modulus of rupture at room temperature was obtained by sintering for 45 minutes at 3900° F. Unetched microstructures of specimens sintered for different time periods at 3900° F shown in figure 7 indicate that with increasing sintering time, there is an increasing tendency for the metallic phase to coalesce; this effect was also observed with increasing sintering temperature. The microstructure of the specimen having a high strength (fig. 7(d)) shows a fine dispersion of metallic phase. Strength decreased when the specimen was sintered for 90 minutes at 3900° F and the microstructure (fig. 7(e)) shows large coalesced particles similar to the structure of the specimen sintered at 4050° F for 5 minutes (fig. 4(c)); both specimens had lower strengths than specimens having smaller particles. This result indicates that with the same ceramal composition, size and distribution of the coalesced particles are important in obtaining optimum-strength properties.

An etched microstructure of the same specimen shown in figure 7(d) (sintered at 3900° F for 45 minutes) is shown in figure 8. The increase in number of dark areas can be attributed to the uncovering of additional metallic particles or pores during the etching process. The metallic phase forms in the grain corners, confirming the formation of zirconium during sintering of these materials.

Additional specimens were fabricated by hot-pressing at 3900° F for 45 minutes in order to evaluate the elevated-temperature modulus of rupture of the ceramal consisting of zirconium carbide and approximately 12.5 percent by weight of columbium. Results of this evaluation are shown in the following table:

Specimen	Sintering time (min)	Sintering temperature (°F)	Density (gm/ml)	Evaluation temperature (°F)	Modulus of rupture (lb/sq in.)
7MC3	45	3900	6.26	2000	19,800 22,500
9MC2	45	3900	6.22	2000	25,200
9MC1	45	3900	6.34	2400	15,900 12,300

A linear decrease in strength with increasing evaluation temperature is shown in figure 9, which is a plot of these data.

The average density of the specimens sintered at 3900° F for 45 minutes was found to be 6.29 grams per milliliter; whereas the calculated density, assuming the formation of a zirconium carbide - columbium carbide solid solution and free zirconium metal, was approximately 6.77 grams per milliliter. Thus, the average density of the specimens was approximately 93 percent of the theoretical density.

CONCLUSIONS

An investigation of the sintering mechanism of a zirconium carbide - columbium ceramal (12.5 percent by weight of columbium) indicated that:

1. Columbium atoms diffuse into the zirconium carbide lattice, displace zirconium atoms, and form columbium carbide and zirconium metal according to the equation:

$$Cb + ZrC \xrightarrow{\text{heat}} CbC + Zr$$

2. Columbium carbide that forms during the reaction completely dissolves in the matrix of zirconium carbide and a homogeneous solid solution of the carbides is formed.

3. The zirconium metal forms in the grain corners of the carbide structure at the sintering temperature of 3900° F.

4. Size and distribution of the metal phase formed during sintering are of importance in obtaining good strength properties and can be controlled by two sintering variables, temperature and time at temperature. The specimen with a fine dispersion of metal has the highest strength.

Lewis Flight Propulsion Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, June 16, 1950.

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TABLE I - STRENGTH AND DENSITY OF HOT-PRESSED ZIRCONIUM CARBIDE - COLUMBIUM CERAMALS

Specimen	Sintering time (min)	Sintering temperature (°F)	Density (gm/ml)	Room-temperature modulus of rupture (lb/sq in.)
4MC1	5	3700	5.77	Improper sintering
4MC2	5	3900	6.15	37,100
4MC4	5	3900	6.05	37,400 32,400
4MC3	5	4050	6.24	32,900 31,000
4MC6	15	3900	6.08	51,000 49,400
5MC4	15	3900	6.14	47,500 52,300
5MC5	30	3900	6.18	45,600 52,800
5MC6	45	3900	6.33	57,800 56,600
9MC2	45	3900	6.22	58,800
6MC1	90	3900	6.29	37,700
6MC2	90	3900	6.22	32,400

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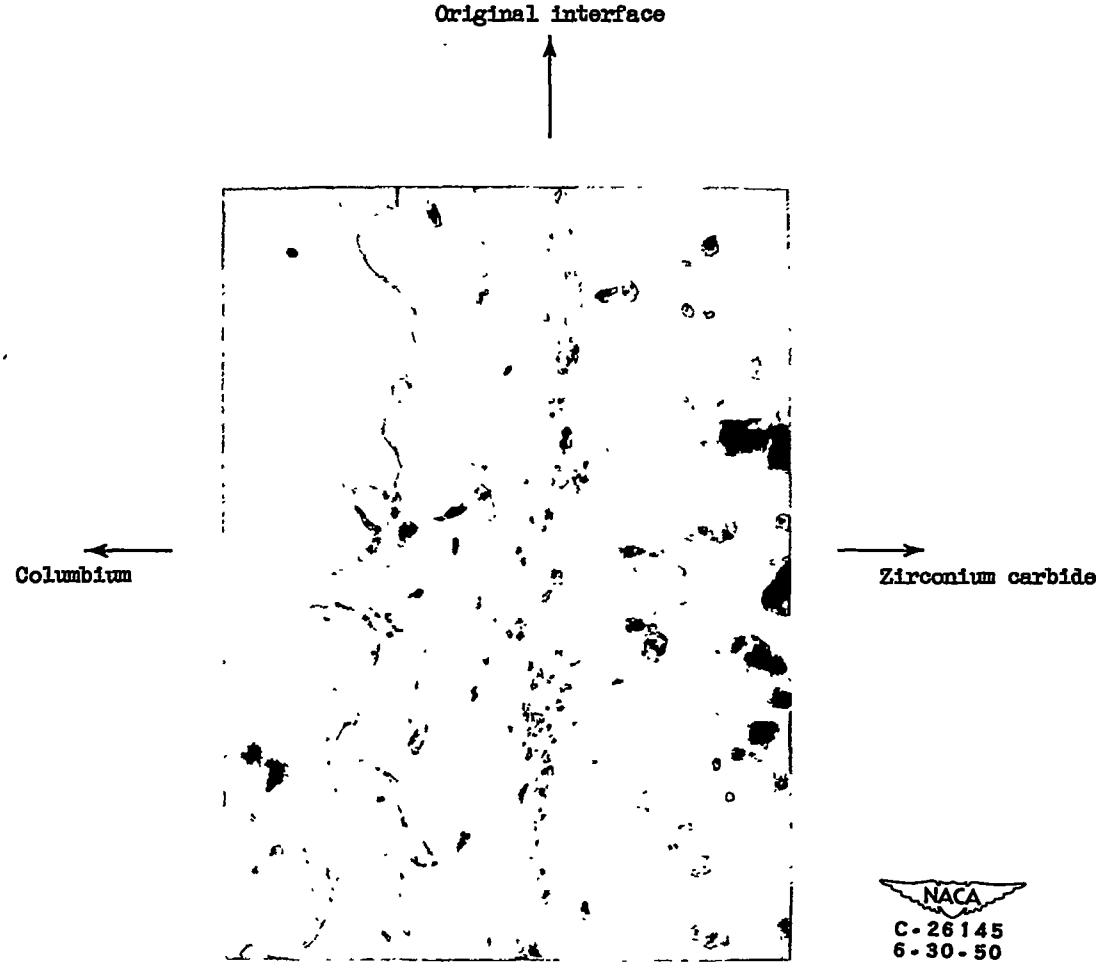


Figure 1. - Microstructure of unetched columbium - zirconium carbide bonding specimen after 15 minutes at 4250° F. X250.

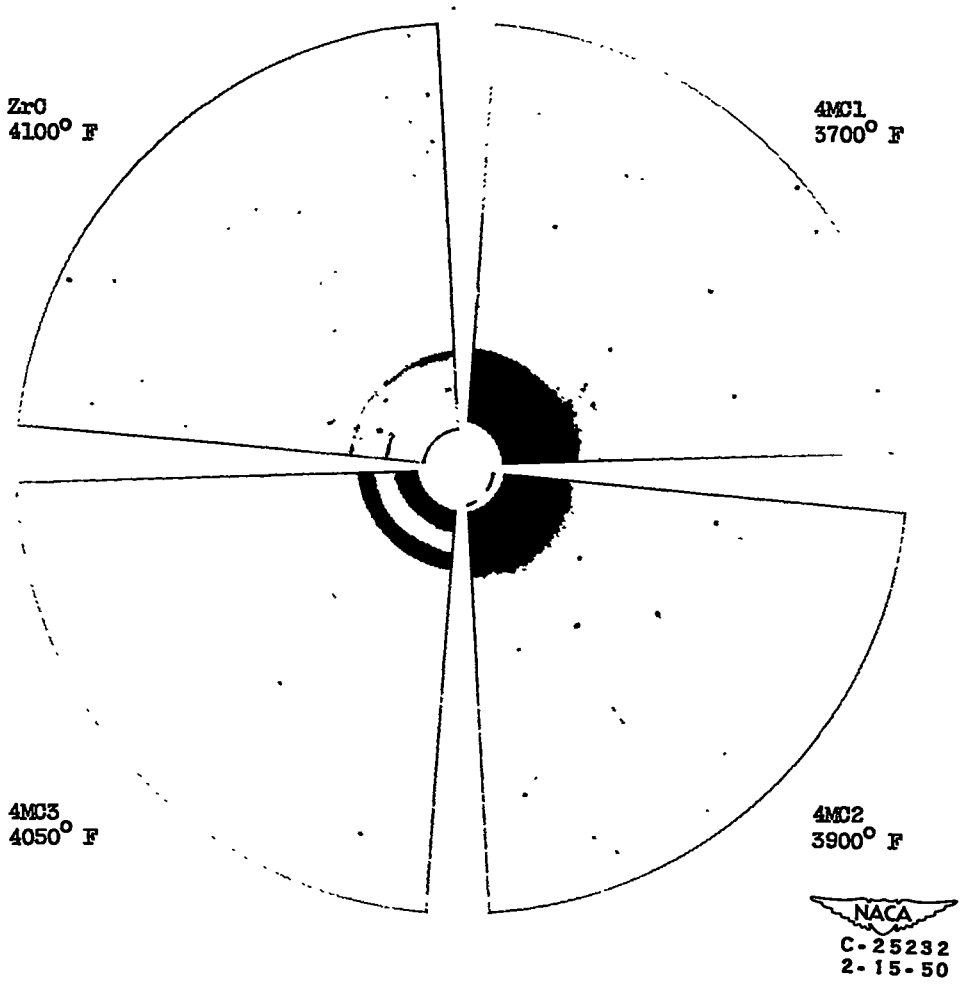


Figure 2. - Back-reflection X-ray diffraction patterns of zirconium carbide - columbium ceramals showing effect of various sintering temperatures on lattice parameters as compared with zirconium carbide. Sintering time, 5 minutes.

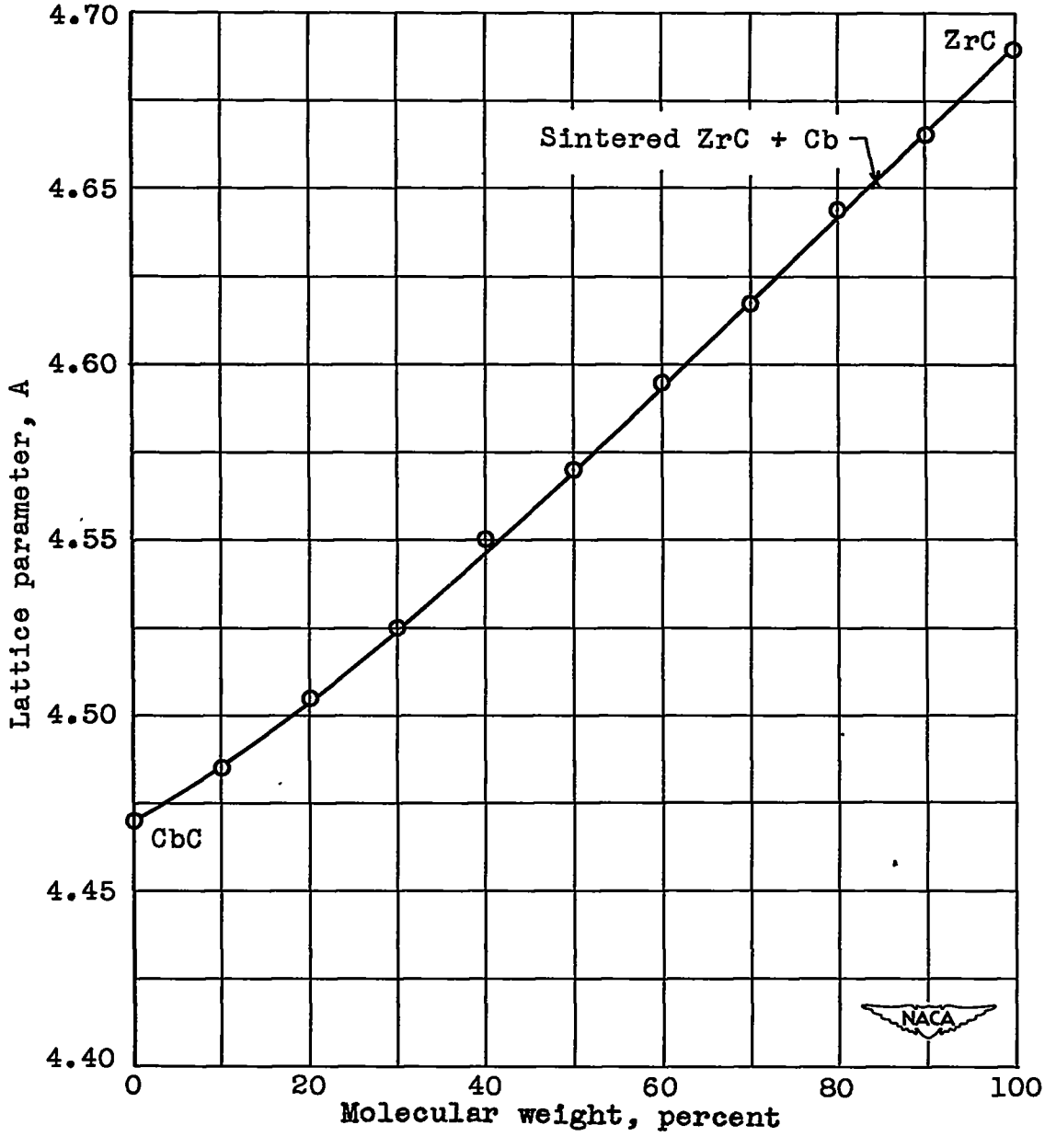
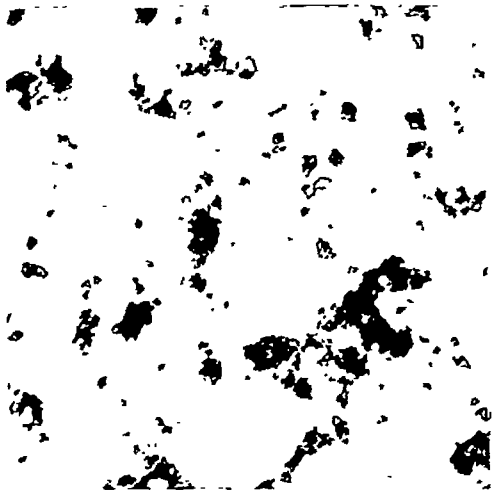
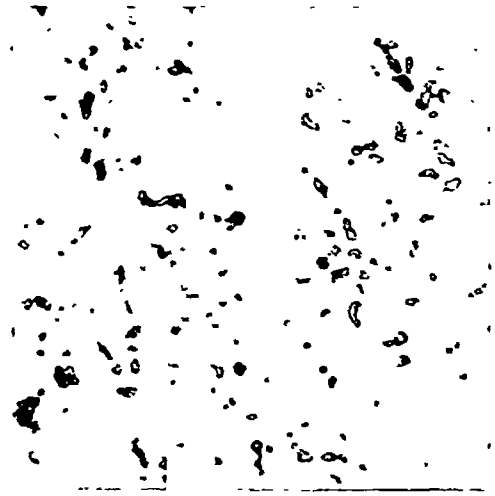


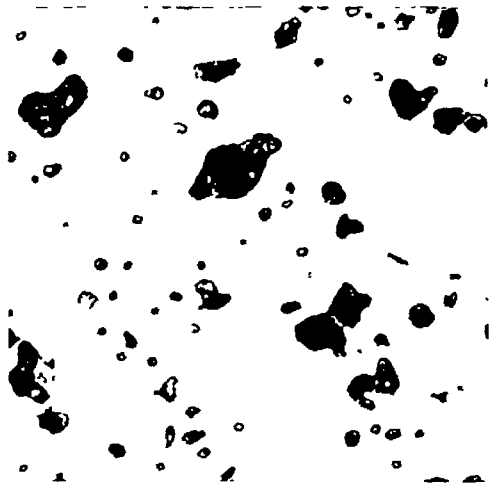
Figure 3. - Lattice-parameter composition curve for columbium carbide plus zirconium carbide. (Data from fig. 2, reference 8.)



(a) 4MC1 sintered at 3700° F.



(b) 4MC2 sintered at 3900° F.



(c) 4MC3 sintered at 4050° F.

Figure 4. - Microstructures of unetched zirconium carbide - columium ceramals showing effect of various sintering temperatures. Sintering time, 5 minutes. X1000.

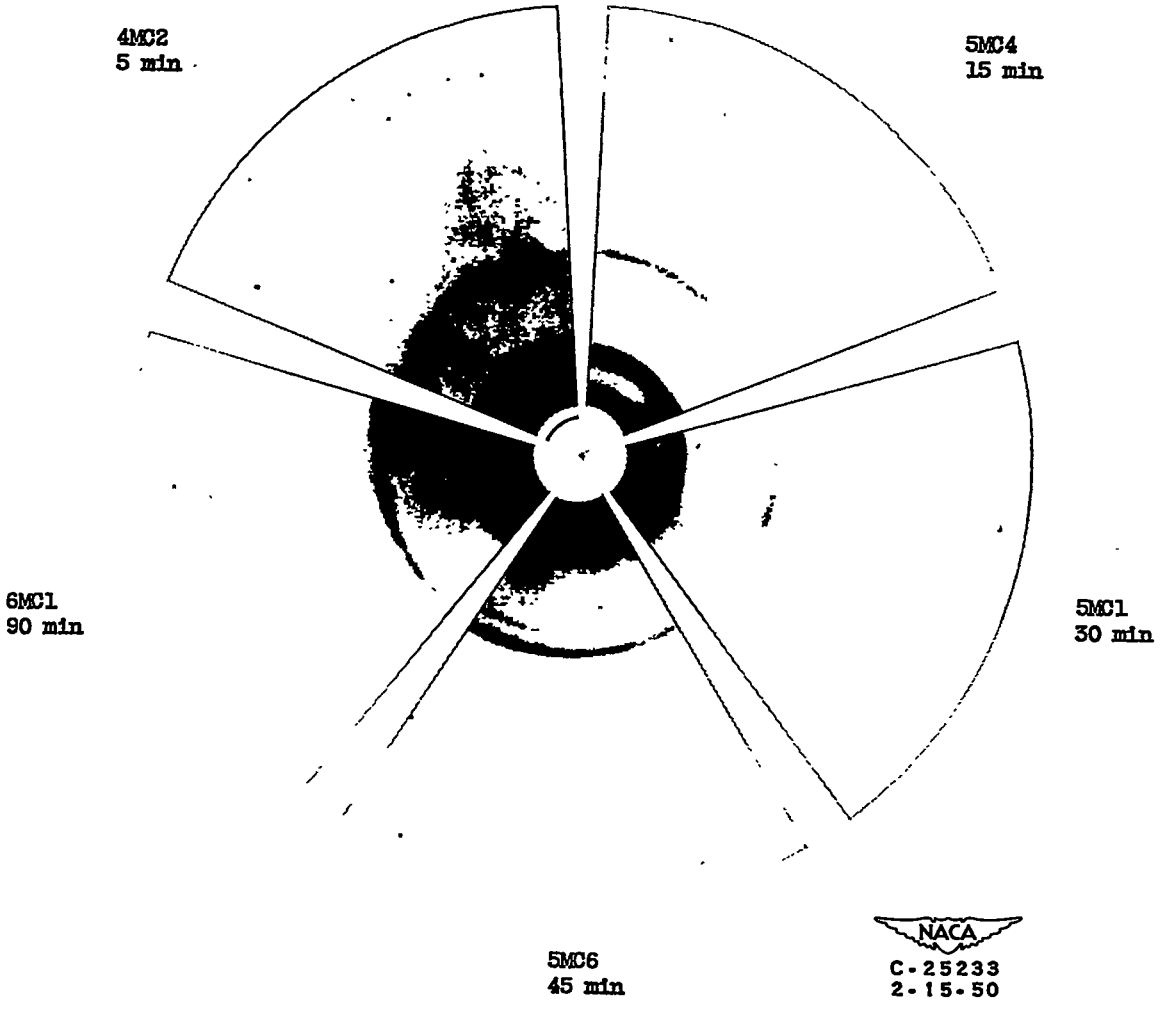


Figure 5. - Back-reflection X-ray diffraction patterns of zirconium carbide - columbium ceramals showing effect of sintering time at 3900° F on lattice parameters.

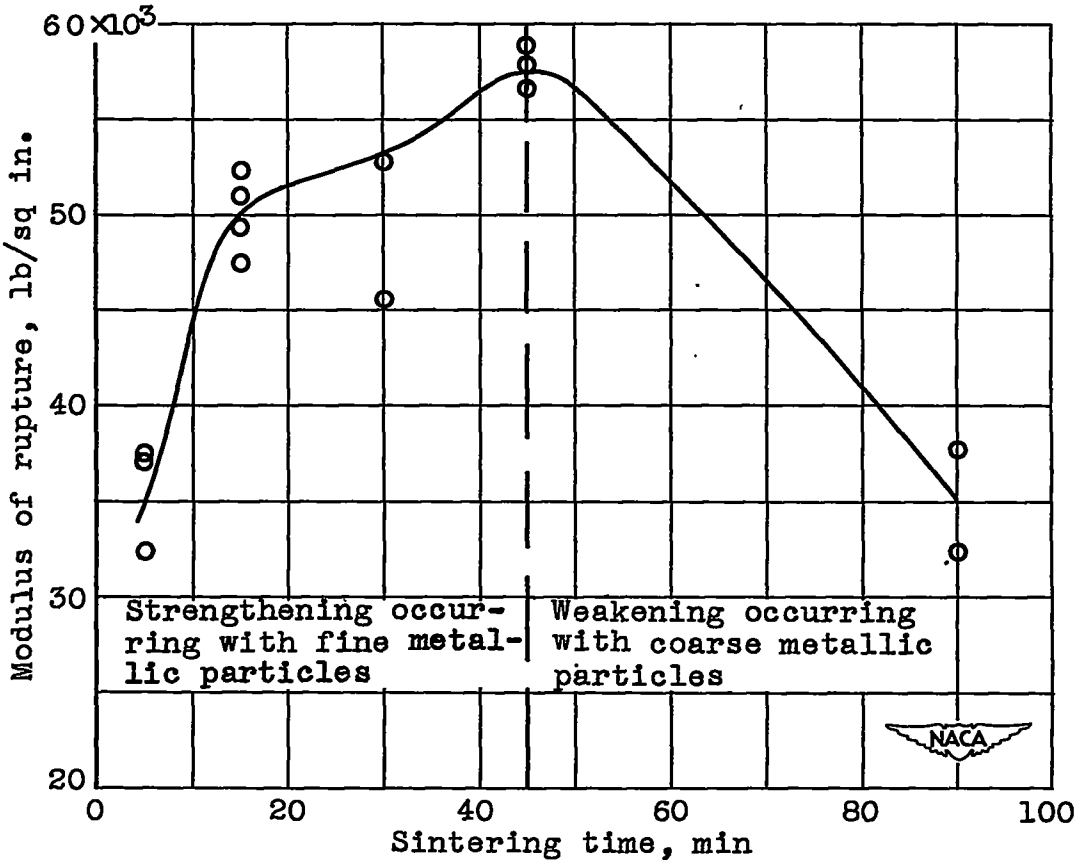
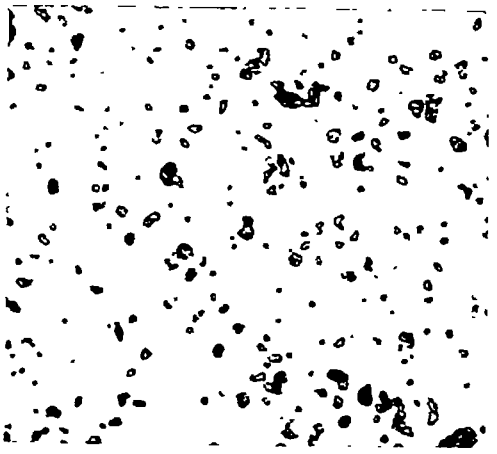
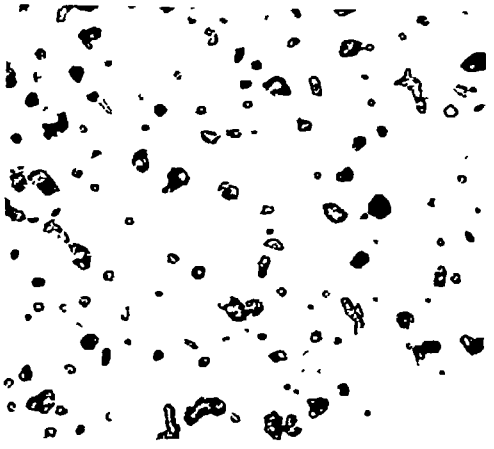


Figure 6. - Variation of room-temperature modulus of rupture with sintering time at 3900° F for zirconium carbide - columbium ceramal.

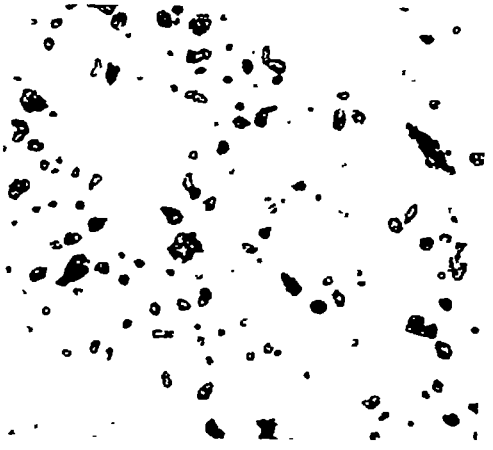
(a) 4MC2 sintered 5 minutes.



(b) 5MC4 sintered 15 minutes.



(c) 5MC5 sintered 30 minutes.



(d) 5MC6 sintered 45 minutes.

(e) 6MC1 sintered 90 minutes.

Figure 7. - Microstructures of unetched zirconium carbide - columbium ceramals showing effect of sintering time at 3900° F. X1000.

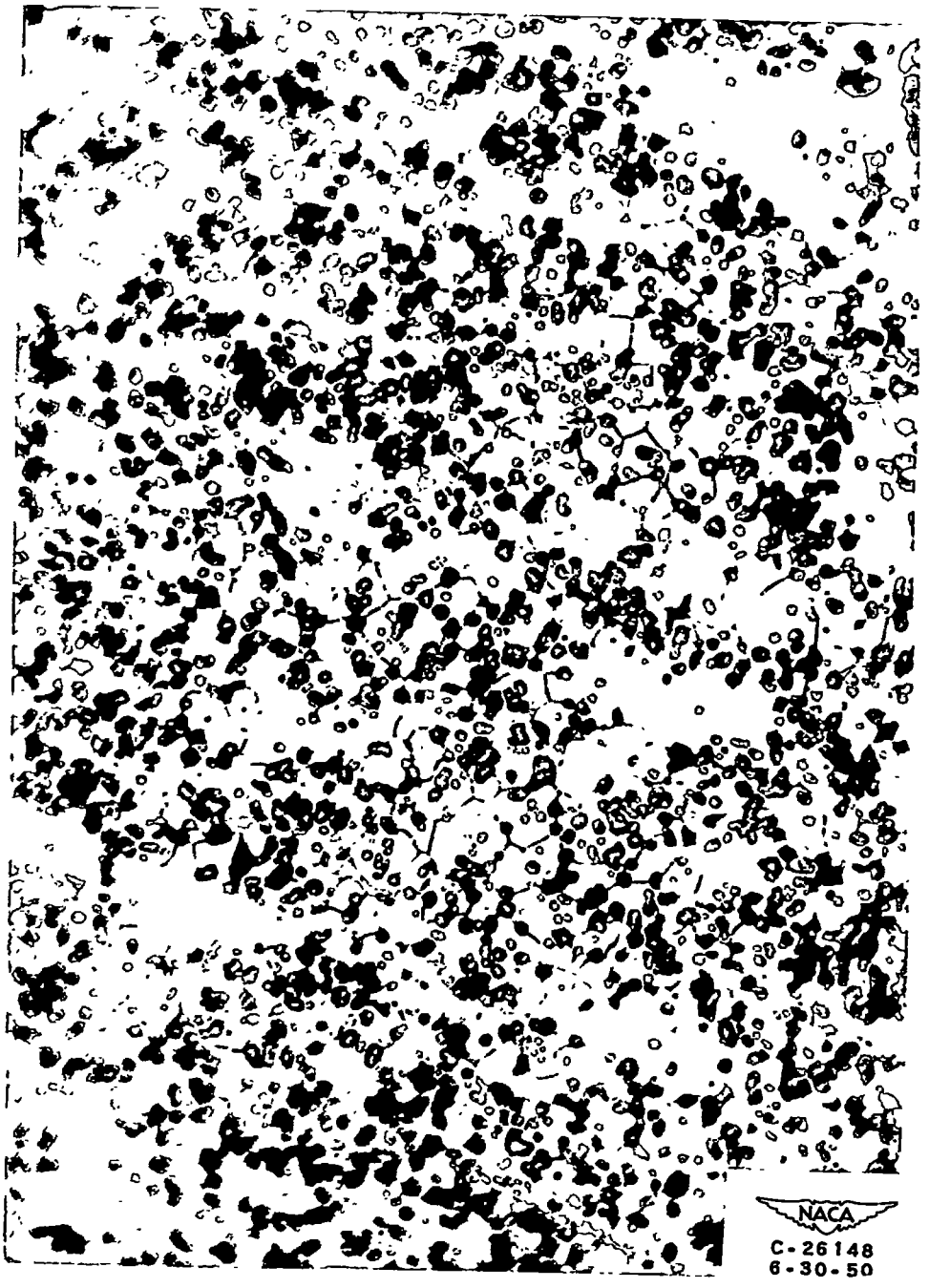


Figure 8. - Microstructure of zirconium carbide - columbium ceramal 5MC6 sintered 3900° F for 45 minutes. Electrolytically etched in equal volumes of saturated solution of chromic acid and concentrated sulphuric acid. X1000.

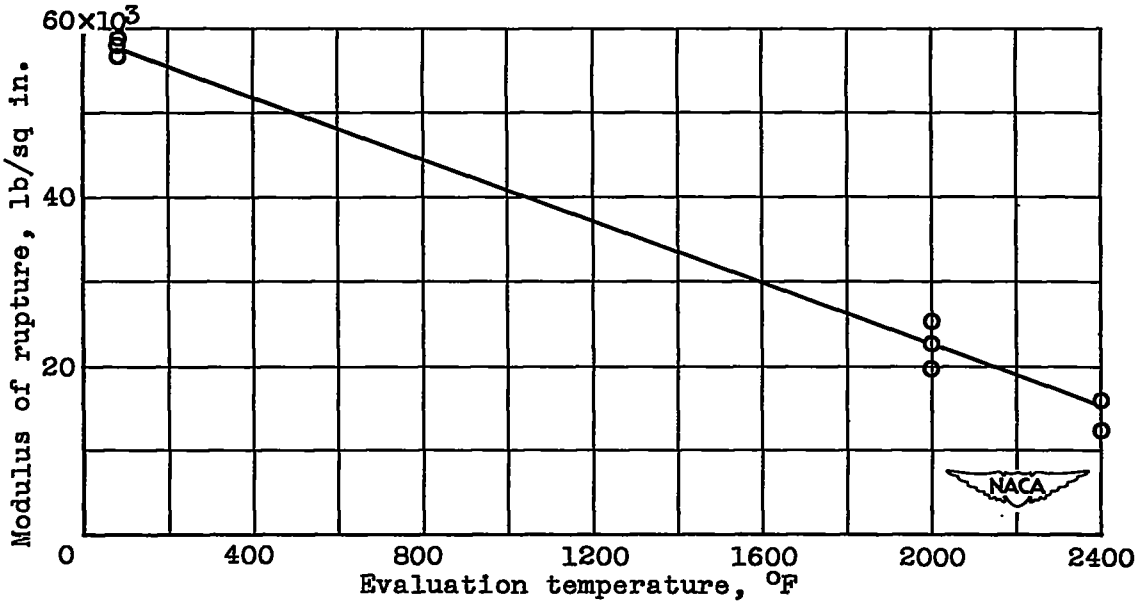


Figure 9. - Variation of modulus of rupture with evaluation temperature for zirconium carbide - columbium ceramal.